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VAPOR PRESSURES AND BOILING POINTS OF SOME PARAFFIN, ALKYL CYCLOPENTANE, ALKYL CYCLOHEX- ANE, AND ALKYL BENZENE HYDROCARBONS¹

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ABSTRACT

Measurements of vapor pressures and boiling points, over the range 47 to 780 millimeters of mercury and above about 12° C, were made on 52 purified hydrocarbons. The apparatus consisted of an electrically heated boiler, a vapor space with a vertical reentrant tube containing a platinum thermometer having a resistance of 25 ohms, and a condenser. Measurements of the temperature of the liquid-vapor equilibrium were made at 20 fixed pressures maintained automatically. The values of the fixed pressures were determined by calibration of the apparatus with water by using the vapor pressure-temperature tables prepared at the National Bureau of Standards.

The experimental data on the hydrocarbons were correlated, the method of least squares being used, with the three-constant Antoine equation for vapor pressures, $\log P = A - B/(C + t)$ or $t = B/(A - \log P) - C$. Experimental data, together with the values of the three constants of the Antoine equation, applicable over the range of measurement, are reported for 30 paraffin, 4 alkylcyclopentane, 10 alkylcyclohexane, and 8 alkylbenzene hydrocarbons.

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I. INTRODUCTION

On 52 purified hydrocarbons, all but 1 of which were prepared in connection with the work of the American Petroleum Institute

¹ This investigation was performed at the National Bureau of Standards jointly by the American Petroleum Institute Research Project 6 on the Analysis, Purification, and Properties of Hydrocarbons and the American Petroleum Institute Research Project 44 on the Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons. This paper contains material to be submitted in a thesis to the University of Maryland by Charles B. Willingham in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The interest and advice of Professor M. M. Haring are gratefully acknowledged.

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Research Project 6 at the National Bureau of Standards, measurements of vapor pressures and boiling points were made over the range 47 to 780 mm Hg and above about 12° C. This paper describes the experimental procedure and apparatus, gives the method of calculation used in correlating the data with the three-constant Antoine equation for vapor pressures, and presents the experimental data and results of the calculations for 30 paraffin, 4 alkylcyclopentane, 10 alkylcyclohexane, and 8 alkylbenzene hydrocarbons, together with some discussion of the results.

II. APPARATUS AND PROCEDURE

For the measurements of temperature, a precision platinum resistance thermometer (25 ohms, Leeds & Northrup Serial No. 318514) and a Müeller-type resistance bridge with thermostated coils (Leeds

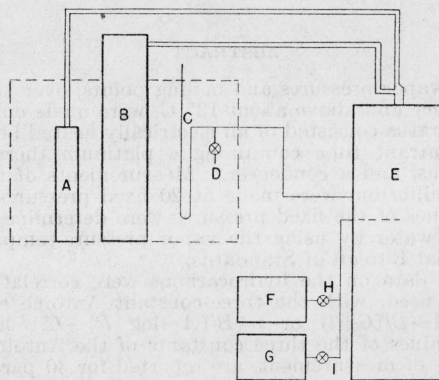


FIGURE 1.—Diagram of the assembly of the boiling-point apparatus.

The letters have the following significance: A, Boiler, etc.; B, mercury manometer for regulating the pressure; C, simple mercury manometer for indicating the pressure in the system; D, valve outlet to the atmosphere; E, gas reservoir for the pressure control system; F, pressure pump; G, vacuum pump; H, I, valves.

& Northrup Serial No. 373146) were used. The thermometric sensitivity was such that 1 mm on the scale was equivalent to 0.0007 degree centigrade.

A diagram and description of the parts of the assembly of the apparatus used in this investigation are given in figure 1.

Details of the boiler and related parts of the apparatus⁴ are shown in figure 2.

The manometer for regulating the pressure at 20 fixed points is shown in figure 3. A detailed view of the top part of the manometer tube is shown in figure 4. The contacts were tungsten, sharply pointed, and shaped as shown in figures 3 and 4. For cleaning the tungsten-point contacts, the manometer tube was filled with a concentrated solution of sodium hydroxide and an alternating current (at 110 volts) was intermittently passed between two contacts at intervals of about 2 seconds until each point contact had a clean metallic appearance. For this latter procedure, the contacts were taken as follows: First and eleventh; second and twelfth; third and

⁴ Since the completion of this investigation, a number of improvements have been made in the boiler part of the apparatus for use in subsequent measurements [14]. One of the improvements consisted in replacing the condenser and reflux regulator with the new design recently described [15].

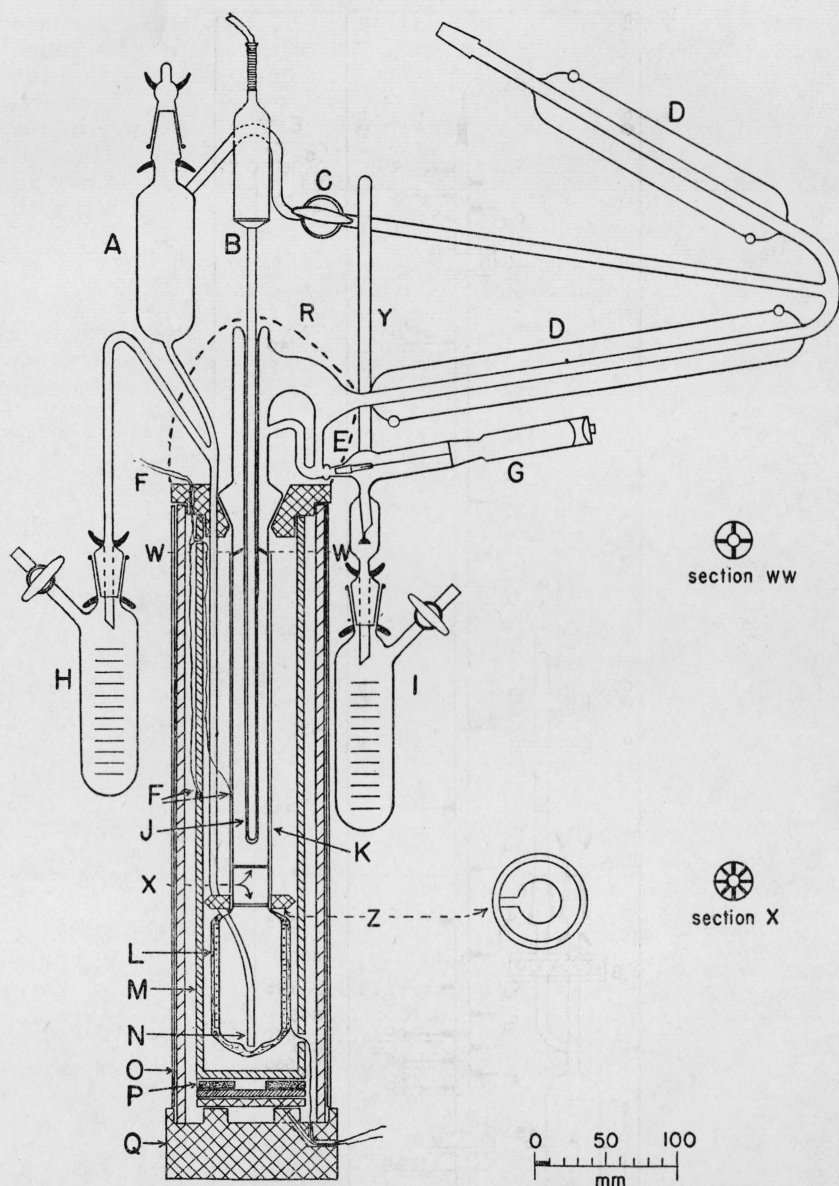


FIGURE 2.—Details of the boiler and related parts of the boiling-point apparatus.

The letters have the following significance: A, Tube through which the sample is introduced; B, platinum resistance thermometer; C, stopcock; D, D, condensers; E, ground glass valve for withdrawing distillate (see reference [1]); F, thermocouple, for measuring difference in temperature between the wall of the glass boiler and the jacket; G, metal control for the ground-glass valve (see reference [1]); H, receiver for recovering sample at the conclusion of the measurements; I, receiver for collecting distillate removed from the head during the experiment; J, glass well for the platinum resistance thermometer; K, radiation shield of aluminum foil; L, electric heater for boiling the liquid in the pot; M, jacket, ¼-in. wall, of aluminum; N, tube for withdrawing sample from the pot; O, thermal insulating jacket, Pyrex glass cylinder with an asbestos layer covered with aluminum foil; P, flat electric heater for the aluminum jacket; Q, transite support; R, thermal insulation, covered with aluminum foil; W, glass rod supports for the thermometer well; X, glass rod, "spiders"; Y, connecting tube for equalizing pressure; Z, transite collar for centering boiler.

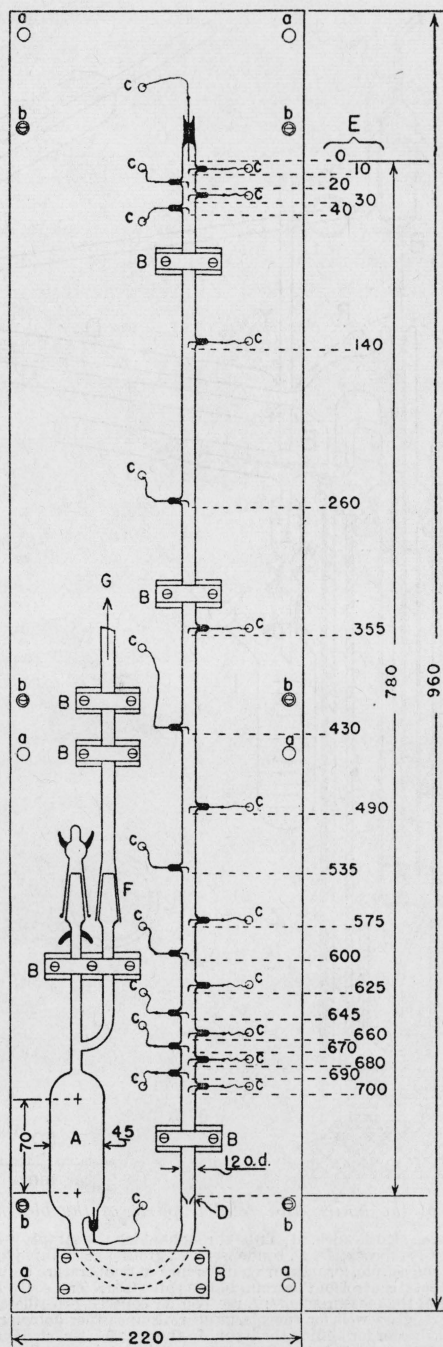


FIGURE 3.—Manometer for regulating the pressure at 20 fixed points.

The letters have the following significance: *A*, Mercury reservoir; *B*, transite blocks; *D*, throat; *E*, approximate distances, in millimeters from the top contact to the other contacts; *F*, glass male to metal female joint (see reference [2]); *G*, connection to pressure system and boiler; *a*, holes for bolts to support frame to wall; *b*, bolts holding transite board to 1 in. channel steel back of board; *c*, holes for electric wire leads. All dimensions shown are in millimeters.

thirteenth; etc. After all the contacts were prepared in this manner, the manometer tube was washed thoroughly with water and dried. The Bureau's Glassblowing Shop evacuated the manometer, baked it at 150° C for about 4 hours, and then distilled into it the appropriate amount of mercury. In the assembly of the manometer, the wiring was arranged so that in the 6-volt direct-current circuit the mercury was positive with respect to the tungsten. In operation, the mercury manometer was encased in an air thermostat. As shown in figure 5, the air thermostat was provided with an electric space heater, a rotary air circulator driven by a motor mounted outside the thermostat, a mercury thermoregulator, and appropriate relays. The temperature

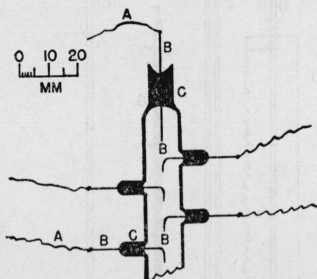


FIGURE 4.—View of the top portion of the manometer tube.

The letters have the following significance: *A*, Copper wire connections to the relay controls (*K* in fig. 6); *B*, tungsten rod (No. 16 AWG), shaped and pointed as shown (see text); *C*, seal of tungsten rod through Pyrex Uranium and Pyrex Clear glass.

inside the air thermostat was maintained constant to about ± 0.02 degree centigrade.

The wiring diagram for the apparatus is shown in figure 6.

For the purpose of making measurements 10 to 15 degrees centigrade below room temperature, in the case of the more volatile compounds, a vacuum-jacketed condenser, cooled to near -80°C with solid carbon dioxide in a 50:50 mixture of carbon tetrachloride and chloroform, was placed between the upper condenser (*D*, fig. 2) and the pressure control system. For such measurements below room temperature, the aluminum jacket (*M*, fig. 2) was cooled to about 10 degrees centigrade below the boiling temperature by means of a stream of air cooled by passing through a coil of metal tubing at -80°C (see above). The cooled air passed into the space between *M* and *O* in figure 2.

The procedure for performing a series of measurements on a given hydrocarbon was as follows:

With appropriate refrigerants having been placed in the condensers, the system for regulating the pressure was set at the lowest contact (pressure near 47 mm Hg),⁵ started, and permitted to adjust itself automatically at this pressure. The stopcock between the boiler and the pressure system was then closed and dry air was let into the boiler part of the apparatus through the stopcock on the receiver (*I*, fig. 2). About 30 to 50 ml of the substance under investigation was introduced into the boiler through the filling tube (*A*, fig. 2). The openings to the atmosphere were then closed, and the stopcock between the boiler and the pressure-control system was opened. The pot heater

⁵ For the more volatile compounds, the lowest pressure of measurement was that corresponding to a temperature of about 12° C.

(*L*, fig. 2) was turned on and adjusted to give a reasonable boiling rate. After equilibrium was established 1 ml of liquid was removed from the condenser through the ground-glass valve (*E*, fig. 2) into the receiver (*I*, fig. 2). This procedure served to remove traces of water that may have gotten into the boiler from the atmosphere during the introduction of the sample. The temperature of the aluminum jacket (*M*, fig. 2) was adjusted to a temperature about 10 degrees centigrade below the boiling temperature.

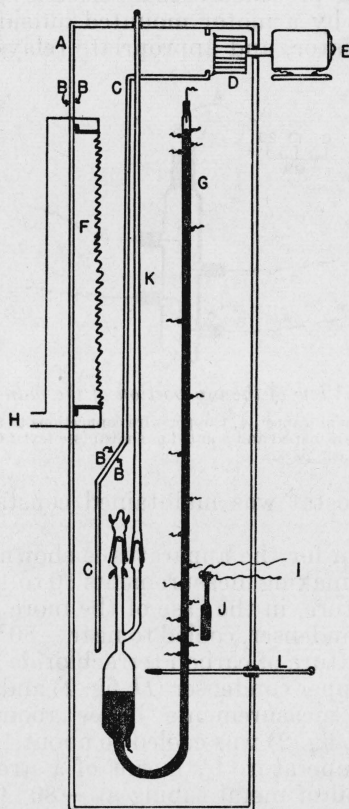


FIGURE 5.—Manometer assembly, showing the air thermostat.

The letters have the following significance: *A*, Box enclosure with walls of transite (the cover is not shown); *B*, aluminum foil, covering inside and outside surface of the transite box; *C*, partial partition wall of transite (both sides covered with aluminum foil) serving to guide the flow of air; *D*, rotary air circulator; *E*, electric motor, mounted independently of the thermostat housing; *F*, electric space heater, 100 watts; *G*, mercury manometer; *H*, connection to electric power through relay contacts (*G* in fig. 6); *I*, connection to relay coil (*G* in fig. 6); *J*, mercury thermoregulator; *K*, connection to pressure system; *L*, mercury-in-glass thermometer.

At each of the 20 contacts in turn, conditioning of the controlling manometer to obtain high reproducibility was made as follows: The pressure was increased about 7 mm above the contact corresponding to the selected pressure by admitting dry air or inert gas through the appropriate valve. The pressure was then reduced to about 7 mm below the contact corresponding to the selected pressure. The pressure was then increased slowly to the selected value where

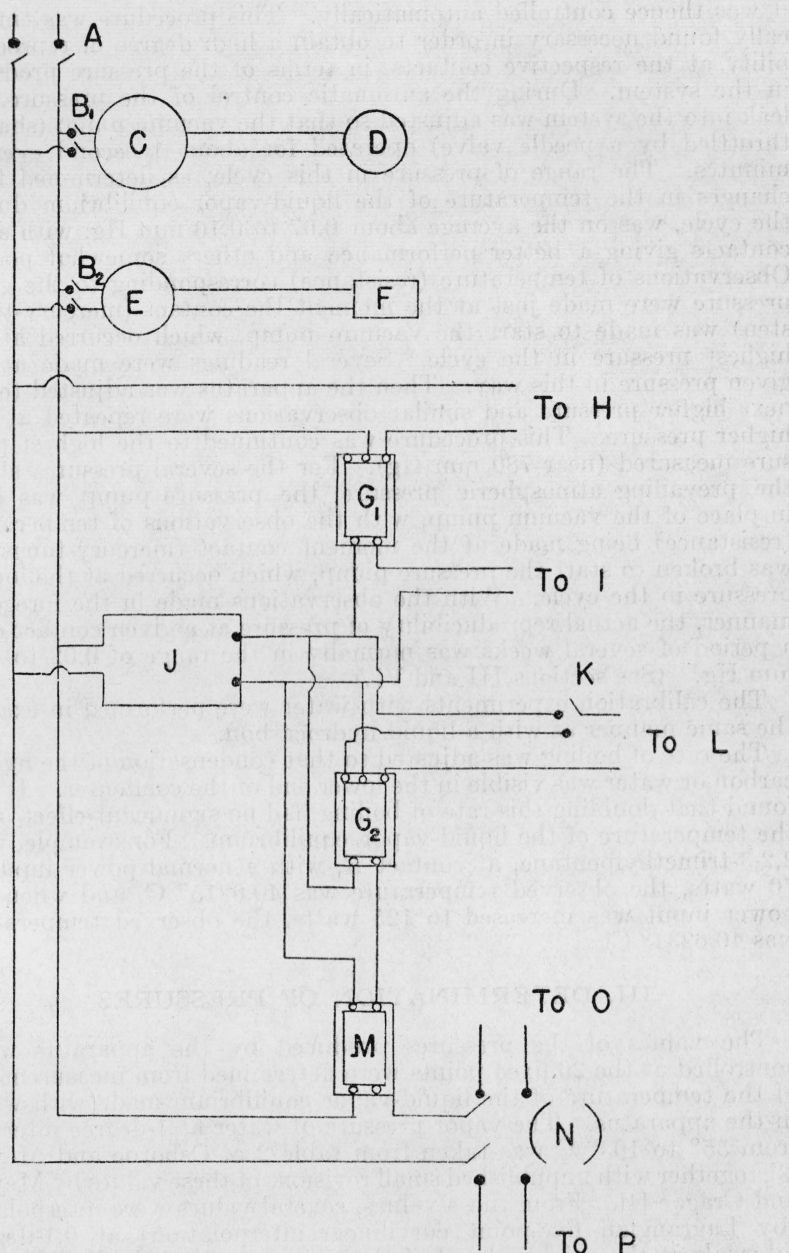


FIGURE 6.—Wiring diagram for boiling-point apparatus.

The letters have the following significance: A, Power from main line; B₁, B₂, double-pole, single-throw switches; C, variable transformer, 750 watts; D, jacket heater; E, variable transformer, 100 watts; F, pot heater; G₁, G₂, small relays, 6 volts, direct current; H, air heater; and I mercury thermoregulator, for controlling air thermostat for main mercury manometer (fig. 3); J, rectifying transformer, 100 volts alternating current to 6 volts, direct current; K, single-pole, double-throw switch; L, 21 contacts for main mercury manometer; M, main relay; N, double-pole, double-throw switch; O, pressure pump; P, vacuum pump.

it was thence controlled automatically. This procedure was empirically found necessary in order to obtain a high degree of reproducibility at the respective contacts, in terms of the pressure produced in the system. During the automatic control of the pressure, the leak into the system was adjusted so that the vacuum pump (sharply throttled by a needle valve) operated for about 1 second every 3 minutes. The range of pressure in this cycle, as determined from changes in the temperature of the liquid-vapor equilibrium during the cycle, was on the average about 0.07 to 0.10 mm Hg, with some contacts giving a better performance and others somewhat poorer. Observations of temperature (resistance) corresponding to the given pressure were made just at the moment the contact (mercury-tungsten) was made to start the vacuum pump, which occurred at the highest pressure in the cycle. Several readings were made at the given pressure in this way. Then the apparatus was adjusted to the next higher pressure and similar observations were repeated at this higher pressure. This procedure was continued to the highest pressure measured (near 780 mm Hg). For the several pressures above the prevailing atmospheric pressure, the pressure pump was used in place of the vacuum pump, with the observations of temperature (resistance) being made at the moment contact (mercury-tungsten) was broken to start the pressure pump, which occurred at the lowest pressure in the cycle. With the observations made in the foregoing manner, the actual reproducibility of pressure at a given contact over a period of several weeks was normally in the range of 0.02 to 0.05 mm Hg. (See sections III and VI.)

The calibration experiments with water were performed in exactly the same manner as with a liquid hydrocarbon.

The rate of boiling was adjusted so that condensation of the hydrocarbon or water was visible in the lower end of the condenser. It was found that doubling this rate of boiling had no significant effect upon the temperature of the liquid-vapor equilibrium. For example, with 2,2,3-trimethylpentane, at contact *R*, with a normal power input of 70 watts, the observed temperature was 40.6215° C, and when the power input was increased to 125 watts, the observed temperature was 40.6231° C.

III. DETERMINATION OF PRESSURES

The values of the pressures produced by the apparatus when controlled at the 20 fixed points were determined from measurements of the temperature of the liquid-vapor equilibrium made with water in the apparatus. The vapor pressure of water at 1-degree intervals from 35° to 103° C was taken from table 2 of Osborne and Meyers [3], together with unpublished small revisions of these values by Meyers and Cragoe [4]. From these values, several values were interpolated (by Lagrangian five-point curvilinear interpolation) at 0.1-degree intervals in the neighborhood of the temperature of the liquid-vapor equilibrium for water at each of the 20 fixed pressures. The final calculation of the pressure at each observed temperature was made by linear interpolation within the 0.1-degree intervals.

Figure 7 is a plot of the observations made with water in the apparatus over the period from November 1941 to May 1943, and shows on an enlarged scale the calculated pressure at each contact

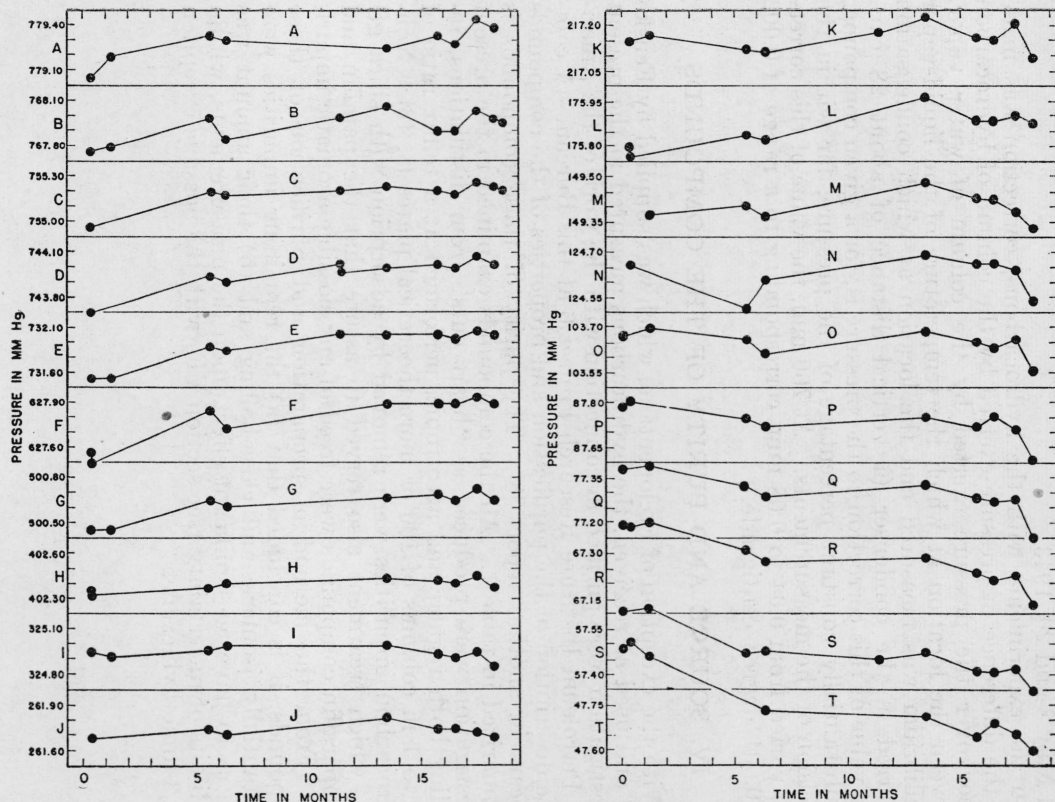


FIGURE 7.—Results obtained with water, as a function of time.

The scale of ordinates gives the pressure calculated from the observed temperature and the vapor-pressure relations for water [3, 4]. The scale of abscissas gives the time in months.

for each observation over this period. The observed points were connected by straight lines, as shown in figure 7, and the pressures to be assigned to the measurements made on a given compound were interpolated from these lines. Calibration measurements were performed on the following dates: November 3, 12, and 13, and December 8 and 9, 1941; April 16, 17, and 20, May 12, October 13 and 15, and December 15, 1942; and February 23, March 16, April 15, and May 8 and 20, 1943.

In the experiments with the hydrocarbons, correction was made for the difference in pressure exerted by the column of hydrocarbon vapor over the pressure exerted by the column of water vapor, between the location at which the temperature of the liquid-vapor equilibrium was measured and the location at which condensation occurred in the condenser (a vertical distance of about 28 cm). The value of this correction to the pressure is, for a given compound, a substantially constant percentage of the pressure, far within the precision of the measurements. At 760 mm, the value of this correction varied from 0.04 to 0.08 mm, corresponding to a range of 0.002 to 0.004 degree centigrade.

IV. SOURCE AND PURITY OF THE COMPOUNDS

With the exception of cyclopentane, which was supplied by Fenske [10] and used as received, the hydrocarbons measured in the present investigation were purified in connection with the work of the American Petroleum Institute Research Project 6 at this Bureau. A complete description of the purification and properties of the compounds appears in another report [8]. The purity of these compounds is summarized in table 1. All the compounds examined in the present investigation were produced as "heart cuts" from distillations, including both regular and azeotropic, performed at a reflux ratio of 100 to 1 in columns of 100 or more theoretical plates [8, 16]. Non-hydrocarbon impurities were removed by adsorption with silica gel [17], which treatment also served to assure that the paraffin and cycloparaffin compounds were freed of any possible aromatic impurities. From the method of preparation and purification of these compounds, it is concluded that (a) the remaining impurities were substantially isomeric and close-boiling and (b) their amount was such as to have no significant effect upon the measurements, within the limits of uncertainty (see section VI), with the possible exception of 2,3-dimethylhexane.

TABLE 1.—Purity of the compounds investigated

[Except for cyclopentane, which was used as received [10], and *n*-dodecane, which was previously prepared [9], all the compounds listed were purified in connection with the work of the API Research Project 6 by means of azeotropic distillation in columns of high efficiency (approximately 100 theoretical plates) at a high reflux ratio (100 to 1) from starting material obtained from various sources [8].]

Compound	Amount of impurity ^a
PARAFFINS	
	<i>Mole fraction</i>
<i>n</i> -Pentane.....	0.0014
2-Methylbutane (isopentane).....	.0054
<i>n</i> -Hexane.....	.0009
2-Methylpentane.....	.0011
3-Methylpentane.....	^b (.0015)
2,2-Dimethylbutane.....	.0006
2,3-Dimethylbutane.....	.0010
<i>n</i> -Heptane.....	.0012
2,2-Dimethylpentane.....	.0002
3,3-Dimethylpentane.....	.0017
<i>n</i> -Octane.....	.0004
2-Methylheptane.....	.010
3-Methylheptane.....	.006
4-Methylheptane.....	.0015
3-Ethylhexane.....	^b (<.02)
2,2-Dimethylhexane.....	.0018
2,3-Dimethylhexane.....	^b (.057)
2,4-Dimethylhexane.....	^b (<.02)
2,5-Dimethylhexane.....	.010
3,3-Dimethylhexane.....	<.005
3,4-Dimethylhexane.....	^b (<.02)
2-Methyl-3-ethylpentane.....	.005
3-Methyl-3-ethylpentane.....	.005
2,2,3-Trimethylpentane.....	.007
2,2,4-Trimethylpentane.....	.0012
2,3,3-Trimethylpentane.....	.0059
2,3,4-Trimethylpentane.....	.0016
<i>n</i> -Nonane.....	<.003
<i>n</i> -Decane.....	<.004
<i>n</i> -Dodecane.....	<.0006
ALKYLCYCLOPENTANES	
Cyclopentane.....	0.0003
Methylcyclopentane.....	.0013
<i>n</i> -Propylcyclopentane.....	<.005
Isopropylcyclopentane.....	.0028
ALKYLCYCLOHEXANES	
Cyclohexane.....	0.0001
Methylcyclohexane.....	.0029
Ethylcyclohexane.....	.0024
<i>cis</i> -1,2-Dimethylcyclohexane.....	.0011
<i>trans</i> -1,2-Dimethylcyclohexane.....	.009
<i>cis</i> -1,3-Dimethylcyclohexane.....	.023
<i>trans</i> -1,3-Dimethylcyclohexane.....	.015
<i>cis</i> -1,4-Dimethylcyclohexane.....	.010
<i>trans</i> -1,4-Dimethylcyclohexane.....	.004
<i>n</i> -Propylcyclohexane.....	<.005
ALKYLBENZENES	
Benzene.....	0.0004
Toluene.....	.0010
Ethylbenzene.....	.0045
<i>o</i> -Xylene.....	.0008
<i>m</i> -Xylene.....	.0028
<i>p</i> -Xylene.....	.0010
<i>n</i> -Propylbenzene.....	.0028
Isopropylbenzene.....	.0004

^a Determined from measurements of freezing points, unless otherwise indicated [8].

^b Estimated by analogy with isomers subjected to similar preparation and purification [8].

V. EXPERIMENTAL DATA ON 52 HYDROCARBONS

In table 2 are given the experimental data on the temperatures and pressures of the liquid-vapor equilibrium, obtained as described in the preceding sections, for the 52 compounds, comprising 30 paraffin, 4 alkylcyclopentane, 10 alkylcyclohexane, and 8 aromatic hydrocarbons. The date of measurement of each compound is also given. In those cases in which two samples of the same compound are included, they are distinguished by the roman numerals I and II.

TABLE 2.—*Experimental data for 52 hydrocarbons on the temperatures and pressures of the liquid-vapor equilibrium*

<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>
<i>n</i> -Pentane March 30, 1943		2-Methylbutane (Isopentane) April 21, 1943		<i>n</i> -Hexane March 31, 1943		2-Methylpen- tane March 25, 1943		3-Methylpen- tane March 26, 1943		2,2-Dimethyl- butane March 24, 1943			
° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg
36.818	779.40	28.587	779.48	69.541	779.41	61.066	779.37	64.083	779.38	50.529	779.38		
36.379	768.01	28.160	768.08	69.081	768.02	60.602	767.99	63.617	768.00	50.074	768.00		
35.890	755.27	27.673	755.31	68.540	755.27	60.074	755.26	63.084	755.26	49.544	755.26		
35.453	744.07	27.240	744.11	68.067	744.09	59.607	744.07	62.610	744.07	49.078	744.07		
34.981	732.09	26.773	732.12	67.554	732.10	59.099	732.09	62.098	732.10	48.575	732.09		
30.592	627.95	22.435	627.97	62.785	627.95	54.388	627.94	57.340	627.94	43.893	627.95		
24.374	500.71	16.291	500.74	56.030	500.72	47.714	500.70	50.598	500.70	37.269	500.71		
18.647	402.46			49.803	402.45	41.567	402.44	44.389	402.45	31.175	402.44		
13.282	324.94			43.967	324.94	35.810	324.93	38.574	324.94	25.472	324.93		
				38.311	261.74	30.237	261.75	32.941	261.75	19.946	261.75		
				33.631	217.19	25.617	217.18	28.270	217.18	^a 15.376	^a 217.18		
				28.528	175.90	20.584	175.90	23.189	175.90				
				24.717	149.41	^a 16.820	^a 149.42	^a 19.393	^a 149.42				
				20.618	124.66	^a 12.758	^a 124.66	^a 15.290	^a 124.66				
				^a 16.576	^a 103.65								
				^a 13.033	^a 87.74								
2,3-Dimethyl- butane March 24, 1943		<i>n</i> -Heptane (I) March 27, 1942		<i>n</i> -Heptane (II) April 10, 1943		2,2-Dimethyl- pentane January 21, 1942		2,2-Dimethyl- pentane January 20, 1943		3,3-Dimethyl- pentane January 6 to 8, 1942			
° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg
58.789	779.37	99.285	779.37	99.289	779.47			80.050	779.35	86.928	779.28		
58.320	767.99	98.773	768.01	98.781	768.08	65.868	500.56	79.550	768.04	86.421	767.89		
57.790	755.26	98.207	755.23	98.217	755.31	59.349	402.37	78.995	755.28				
57.317	744.07	97.702	743.96	97.710	744.11	53.255	324.96	78.496	744.07	85.335	743.84		
56.806	732.09	97.154	731.99	97.160	732.12	47.348	261.72	77.959	732.11	84.780	731.87		
52.060	627.94	92.053	627.85	92.060	627.98	42.445	217.17	72.958	627.94	79.651	627.67		
45.339	500.71	84.823	500.66	84.832	500.75	37.120	175.81	65.879	500.72	72.384	500.54		
39.150	402.44	78.169	402.39	78.169	402.47	33.151	149.40	59.362	402.46	65.697	402.37		
33.357	324.93	71.930	324.97	71.926	324.94	28.870	124.60	53.261	324.99	59.440	324.94		
27.746	261.75	65.882	261.75	65.877	261.74	24.676	103.69	47.359	261.79	53.370	261.72		
23.099	217.18	60.862	217.14	60.859	217.22	20.989	87.78	42.454	217.21	48.340	217.17		
^a 18.044	^a 175.90	55.394	175.84	55.400	175.91	18.246	77.37	37.129	175.94	42.872	175.80		
^a 14.256	^a 149.42	51.320	149.41	51.320	149.40			33.160	149.46	38.790	149.39		
		46.929	124.54	46.929	124.65			28.879	124.68	34.406	124.61		
		42.599	103.67	42.597	103.66			24.670	103.68	30.086	103.70		
		38.822	87.76	38.795	87.72			20.979	87.74	26.318	87.79		
		36.017	77.34	35.993	77.28			18.253	77.31	23.521	77.38		
		33.024	67.33	32.973	67.22			15.325	67.27	20.533	67.39		
		29.699	57.49	29.648	57.42					17.221	57.58		
		25.925	47.78	25.827	47.66					13.443	47.88		

^a This point was not used in the evaluation of the constants *A*, *B*, and *C* of the Antoine equation.

TABLE 2.—Experimental data for 52 hydrocarbons on the temperatures and pressures of the liquid-vapor equilibrium—Continued

<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>
3, 3-Dimethylpentane January 21, 1943		n-Octane (I) February 23, 1942		n-Octane (II) December 31, 1942		2-Methylheptane (I) February 6, 1942		2-Methylheptane (II) December 23, 1942		3-Methylheptane (I) April 2, 1942	
° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg
86.429	768.03	126.570	779.32	126.040	768.09	118.544	779.31	118.020	768.11	119.814	779.37
85.854	755.28	126.035	767.96	125.442	755.29	118.022	767.94	117.427	755.29	119.283	768.01
85.344	744.07	124.899	755.03	124.906	744.06	117.426	755.00	116.895	744.06	118.693	755.08
84.792	732.11	124.319	743.92	124.327	732.11	116.888	743.74	116.319	732.11	118.160	743.98
		118.924	627.77			116.318	731.92			117.584	731.97
		111.277	500.61			110.971	627.73			112.217	627.85
		104.233	402.38			103.397	500.58			104.616	500.66
59.444	324.98	97.635	324.97	97.633	325.00	96.422	402.38			97.615	402.39
53.385	261.79	91.230	261.73	91.235	261.81	89.892	324.96			91.057	324.98
		85.916	217.16			83.549	261.73			84.698	261.75
		80.134	175.82			78.278	217.16			79.418	217.14
38.804	149.46	75.820	149.40	75.825	149.48	72.580	175.81			73.676	175.84
34.355	124.68	71.163	124.57	71.171	124.69	68.308	149.40	68.306	149.48	69.372	149.41
		66.587	103.68			63.711	124.59	63.703	124.70	64.775	124.53
		62.592	87.77			59.192	103.69			60.243	103.67
		59.616	77.36			55.229	87.78			55.265	87.76
20.484	67.27	56.456	67.35	56.407	67.29	52.301	77.36			53.317	77.33
17.163	57.44	52.927	57.53	52.874	57.46	49.165	67.47	49.100	67.29	50.171	67.33
						45.687	57.55	45.612	57.46	46.672	57.48
						41.707	47.84			42.672	47.78
3-Methylheptane (II) December 30, 1942		4-Methylheptane (I) April 7, 1942		4-Methylheptane (II) December 22, 1942		3-Ethylhexane December 9, 1942		2,2-Dimethylhexane November 19, 1942		2,3-Dimethylhexane November 25, 1942	
° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg
119.299	768.09	118.605	779.38	118.084	768.11	119.439	779.32	107.731	779.31	116.512	779.31
118.703	755.29	118.079	768.02	117.489	755.29	118.911	768.12	107.209	768.09	115.985	768.10
118.169	744.06	117.483	755.09	116.958	744.06	118.311	755.29	106.619	755.28	115.384	755.29
117.593	732.11	116.949	743.98	116.383	732.11	117.777	744.05	106.095	744.04	114.849	744.05
		116.376	731.96			117.200	732.12	105.526	732.11	114.271	732.12
		111.029	627.87			111.829	627.93	100.234	627.92	108.895	627.92
		103.453	500.67			104.217	500.70	92.741	500.70	101.278	500.70
91.060	325.00	96.475	402.40	89.943	325.00	97.204	402.46	85.839	402.46	94.262	402.46
84.707	261.81	89.943	324.98	83.610	261.82	90.634	325.01	79.379	325.01	87.690	325.01
		83.347	261.75			84.274	261.83	73.128	261.82	81.327	261.82
		78.347	217.14			78.985	217.24	67.935	217.22	76.044	217.23
69.400	149.48	72.620	175.84	68.360	149.48	73.247	175.97	62.292	175.96	70.293	175.96
64.783	124.69	68.348	149.41	63.760	124.70	68.957	149.49	58.082	149.47	66.010	149.48
		63.746	127.53			64.331	124.70	53.546	124.69	61.889	124.69
		59.220	103.67			59.784	103.69	49.087	103.69	56.842	103.69
		55.261	87.76			55.794	87.76	45.173	87.75	52.857	87.75
50.134	67.28	52.314	77.33	49.152	67.29	52.846	77.33	42.278	77.33	49.917	77.33
46.630	57.46	49.183	67.32	45.662	57.47	49.673	67.29	39.179	67.29	46.750	67.29
		45.694	57.48			46.165	57.47	35.747	57.46	43.245	57.46
		41.706	47.77			42.144	47.71	31.814	47.71	39.239	47.71
2,4-Dimethylhexane December 1, 1942		2,5-Dimethylhexane December 2, 1942		3,3-Dimethylhexane November 27, 1942		3,4-Dimethylhexane December 8, 1942		2-Methyl-3-ethylpentane December 10, 1942		3-Methyl-3-ethylpentane December 17, 1942	
° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg
110.323	779.31	110.000	779.31	112.877	779.31	118.638	779.31	116.565	779.31	119.189	779.31
109.801	768.11	109.474	768.11	112.349	768.10	118.108	768.12	116.035	768.12	118.648	768.12
109.209	755.29	108.881	755.29	111.745	755.29	117.500	755.29	115.420	755.29	118.031	755.29
108.681	744.05	108.356	744.05	111.208	744.05	116.962	744.05	114.888	744.05	117.482	744.06
108.109	732.12	107.788	732.12	110.628	732.12	116.382	732.12	114.306	732.12	116.889	732.12
102.802	627.93	102.502	627.93	105.232	627.92	110.971	627.93	108.902	627.93	111.376	627.94
95.284	500.70	95.011	500.70	97.590	500.70	103.305	500.70	101.245	500.70	103.564	500.70
88.358	402.46	88.109	402.46	90.552	402.46	96.246	402.46	94.195	402.46	96.369	402.46
81.874	325.02	81.651	325.01	83.961	325.01	89.633	325.01	87.590	325.01	89.632	325.01
75.596	261.82	75.398	261.82	77.579	261.82	83.230	261.83	81.198	261.83	83.109	261.83
70.383	217.23	70.200	217.23	72.282	217.23	77.910	217.24	75.888	217.24	77.693	217.24
64.715	175.97	64.552	175.97	66.521	175.96	72.126	175.97	70.114	175.97	71.801	175.97
60.489	149.48	60.341	149.48	62.228	149.48	67.810	149.49	65.810	149.49	67.404	149.49
55.933	124.70	55.802	124.70	57.598	124.69	63.158	124.70	61.168	124.70	62.665	124.70
51.452	103.69	51.331	103.69	53.041	103.69	58.579	103.69	56.588	103.69	58.002	103.69
47.523	87.76	47.416	87.76	49.049	87.76	54.571	87.76	52.592	87.76	53.018	87.76
44.615	77.33	44.517	77.33	46.093	77.33	51.598	77.33	49.632	77.33	50.896	77.33
41.502	67.29	41.411	67.29	42.930	67.29	48.413	67.29	46.453	67.29	47.855	67.29
38.048	57.47	37.972	57.47	39.407	57.47	44.882	57.47	42.935	57.47	44.064	57.47
34.092	47.71	34.028	47.71	35.402	47.71	40.832	47.71	38.903	47.71	39.950	47.71

TABLE 2.—*Experimental data for 52 hydrocarbons on the temperatures and pressures of the liquid-vapor equilibrium—Continued*

<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>
2, 2, 3-Tri- methylpentane May 12, 1943		2, 2, 4-Tri- methylpentane (I) March 25, 1942		2, 2, 4-Tri- methylpentane (II) April 13, 1943		2, 3, 3-Tri- methylpentane November 18, 1942		2, 3, 4-Tri- methylpentane December 3, 1942		<i>n</i> -Nonane April 28, 1943	
° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg
110.757	779.43	100.130	779.37	100.138	779.50	115.688	779.31	114.381	779.31	151.754	779.47
110.221	768.03	99.607	768.02	99.610	768.10	115.144	768.09	113.852	768.11	151.195	768.07
109.618	755.29	99.014	755.22	99.022	755.32	114.532	755.28	113.241	755.29	150.565	755.31
109.078	744.08	98.487	743.97	98.495	744.13	113.985	744.04	112.703	744.05	150.002	744.11
108.496	732.11	97.917	731.99	97.926	732.14	113.392	732.11	112.121	732.12	149.394	732.13
103.085	627.93	92.624	627.84	92.634	627.98	107.895	627.92	106.702	627.93	143.738	627.96
95.422	500.69	85.131	500.65	85.141	500.76	100.107	500.70	99.028	500.70	135.721	500.72
88.362	402.39	78.232	402.39	78.240	402.47	92.931	402.46	91.960	402.46	128.329	402.43
81.752	324.86	71.778	324.98	71.781	324.97	86.215	325.01	85.341	325.01	121.399	324.92
75.354	261.69	65.523	261.75	65.524	261.73	79.713	261.82	78.935	261.82	114.684	261.71
70.050	217.09	60.342	217.15	60.346	217.22	74.313	217.22	73.616	217.23	109.115	217.16
64.282	175.88	54.698	175.84	54.711	175.91	68.447	175.96	67.855	175.97	103.047	175.90
59.972	149.33	50.146	149.41	50.505	149.39	64.068	149.47	63.517	149.48	98.491	149.36
55.339	124.53	45.975	124.54	45.977	124.65	59.347	124.69	58.805	124.70	93.610	124.69
50.767	103.54	41.517	103.68	41.519	103.67	54.711	103.69	54.290	103.69	88.801	103.61
46.768	87.60	37.628	87.76	37.609	87.72	50.645	87.75	50.280	87.75	84.582	87.60
43.800	77.13	34.746	77.34	34.722	77.28	47.635	77.33	47.305	77.33	81.458	77.21
40.622	67.12	31.668	67.33	31.620	67.23	44.412	67.29	44.127	67.29	78.097	67.17
37.119	57.33	28.249	57.49	28.201	57.42	40.842	57.47	40.606	57.47	74.388	57.38
33.094	47.59	24.358	47.79	24.274	47.66	36.752	47.71	36.568	47.71	70.127	47.62
<i>n</i> -Decane April 30, 1943		<i>n</i> -Dodecane May 6, 1942		Cyclopentane April 20, 1943		Methylcyclo- pentane April 6, 1943		<i>n</i> -Propylcyclo- pentane May 14, 1943		Isopropyl- cyclopentane May 11, 1943	
° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg
175.121	779.47	217.345	779.39	50.031	779.47	72.634	779.44	131.878	779.42	127.359	779.44
174.538	768.07	216.712	767.95	49.587	768.07	72.150	768.05	131.326	768.03	126.810	768.04
173.882	755.32	216.006	755.10	49.073	755.30	71.612	755.29	130.706	755.28	126.182	755.29
173.295	744.11	215.383	743.98	48.621	744.10	71.128	744.10	130.152	744.07	125.625	744.08
172.661	732.13	214.709	732.02	48.131	732.12	70.604	732.11	129.554	732.11	125.024	732.11
166.772	627.97	208.417	627.81	43.574	627.97	65.739	627.96	123.991	627.93	119.431	627.94
158.419	500.72	199.488	500.67	37.119	500.74	58.847	500.73	116.108	500.67	111.508	500.68
150.718	402.44	191.255	402.44	31.172	402.45	52.499	402.46	108.840	402.38	104.204	402.39
143.495	324.91	183.537	325.01	25.598	324.94	46.552	324.95	102.028	324.85	97.363	324.87
136.499	261.71	176.039	261.73	20.196	261.71	40.791	261.74	95.437	261.69	90.734	261.70
130.690	217.15	169.814	217.13	15.707	217.19	36.013	217.20	89.964	217.09	85.237	217.11
124.372	175.90	163.030	175.84	30.816	175.91	30.816	175.91	84.007	175.88	79.265	175.89
119.640	149.36	157.986	149.39	26.935	149.40	26.935	149.40	79.559	149.32	74.788	149.33
114.540	124.58	152.529	124.59	22.757	124.65	22.757	124.65	74.768	124.52	69.971	124.54
109.526	103.60	147.152	103.63	18.642	103.66	18.642	103.66	70.042	103.54	65.234	103.56
105.118	87.65	142.444	87.73	15.035	87.73	15.035	87.73	65.896	87.59	61.071	87.61
101.839	77.20	138.962	77.30					62.897	77.13	57.999	77.15
98.352	67.16	135.223	67.29					59.539	67.11	54.694	67.12
94.481	57.37	131.108	57.48					55.904	57.33	51.065	57.34
		126.381	47.74					51.737	47.59	46.880	47.59
Cyclohexane April 14, 1943		Methylcyclo- hexane April 7, 1943		Ethylcyclo- hexane April 22, 1943		<i>cis</i> -1,2-Di- methylcyclo- hexane February 16, 1943		<i>trans</i> -1,2-Di- methylcyclo- hexane February 9, 1943		<i>cis</i> -1,3-Di- methylcyclo- hexane February 17, 1943	
° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg
81.682	779.49	101.832	779.46	132.742	779.48	130.684	779.38	124.372	779.31	125.391	779.39
81.093	768.09	101.312	768.05	132.181	768.09	130.125	767.98	123.810	768.00	124.841	767.97
80.634	755.32	100.715	755.29	131.551	755.31	129.491	755.27	123.183	755.27	124.218	755.27
80.037	744.13	100.185	744.10	130.988	744.12	128.926	744.08	122.622	744.08	123.661	744.08
79.502	732.13	99.614	732.12	130.379	732.13	128.315	732.11	122.016	732.11	123.061	732.11
74.520	627.98	94.299	627.96	124.723	627.97	122.639	627.94	116.384	627.94	117.475	627.94
67.467	500.76	86.771	500.74	116.709	500.74	114.600	500.73	108.407	500.72	109.562	500.73
60.969	402.48	79.840	402.46	109.327	402.46	107.192	402.45	101.057	402.45	102.274	402.45
54.884	324.96	73.349	324.95	102.412	324.93	100.258	324.96	94.178	324.97	95.450	324.97
48.991	261.73	67.067	261.74	95.716	261.72	93.548	261.76	87.519	261.77	88.842	261.76
44.108	217.22	61.857	217.20	90.158	217.19	87.974	217.18	81.991	217.19	83.362	217.18
38.798	175.91	56.194	175.91	84.115	175.90	81.921	175.90	75.979	175.91	77.402	175.90
34.821	149.39	51.964	149.40	79.587	149.38	77.402	149.44	71.497	149.45	72.958	149.44
30.556	124.65	47.407	124.65	74.738	124.62	72.593	124.67	66.064	124.68	68.168	124.67
26.347	103.67	42.929	103.66	69.948	103.64	67.742	103.66	61.910	103.67	63.453	103.67
22.657	87.72	38.908	87.73	65.755	87.69	63.543	87.73	57.748	87.73	59.316	87.73
19.915	77.28	36.089	77.28	62.655	77.25	60.423	77.29	54.608	77.30	56.261	77.29
		32.976	67.22	59.315	67.20	57.004	67.25	51.365	67.25	52.983	67.25
		29.533	67.42	55.636	67.40	53.413	67.42	47.710	67.42	49.351	67.42
		25.586	47.66	51.412	47.64	49.185	47.65	43.520	47.66	45.195	47.65

* This point was not used in the evaluation of the constants *A*, *B*, and *C* of the Antoine equation.

TABLE 2.—Experimental data for 52 hydrocarbons on the temperatures and pressures of the liquid-vapor equilibrium—Continued

<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>	<i>t</i>	<i>P</i>
<i>trans</i> -1,3-Di-methylcyclo-hexane February 11, 1943		<i>cis</i> -1,4-Di-methylcyclo-hexane February 18, 1943		<i>trans</i> -1,4-Di-methylcyclo-hexane February 12, 1943		<i>n</i> -Propylcyclo-hexane April 27, 1943		Benzene March 10, 1943		Toluene March 11, 1943	
° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg
121.026	779.38	125.263	779.39	120.293	779.39	157.714	779.47	80.922	779.34	111.509	779.34
120.479	767.99	124.712	767.97	119.739	767.99	157.128	768.07	80.442	767.94	110.991	767.95
119.856	755.27	124.089	755.27	119.117	755.27	156.468	755.31	79.898	755.23	110.403	755.24
119.803	744.08	123.530	744.08	118.561	744.08	155.879	744.11	79.413	744.04	109.879	744.05
118.706	732.11	122.929	732.11	117.964	732.11	155.242	732.13	78.891	732.07	109.312	732.08
113.153	627.94	117.330	627.94	112.385	627.94	149.322	627.96	74.028	627.93	104.037	627.93
105.286	500.73	109.397	500.73	104.487	500.73	140.930	500.72	67.135	500.69	96.559	500.68
98.044	402.45	102.094	402.45	97.212	402.45	133.201	402.44	60.784	402.42	89.667	402.43
91.260	324.97	95.255	324.98	90.403	324.98	125.962	324.92	54.832	324.93	83.202	324.93
84.694	261.77	88.636	261.76	83.812	261.77	118.947	261.71	49.066	261.75	76.942	261.75
79.241	217.19	83.141	217.18	78.338	217.19	113.124	217.17	44.284	217.16	71.738	217.16
73.319	175.91	77.170	175.90	72.392	175.91	106.796	175.90	39.078	175.89	66.079	175.89
68.896	149.45	72.708	149.44	67.957	149.45	102.064	149.36	35.191	149.43	61.851	149.43
64.135	124.68	67.911	124.67	63.183	124.67	96.973	124.60	31.004	124.67	57.293	124.67
59.444	103.67	63.186	103.67	58.480	103.67	91.955	103.62	26.886	103.64	52.802	103.64
55.334	87.73	59.045	87.73	54.364	87.73	87.555	87.67	23.270	87.75	48.867	87.75
52.298	77.30	55.984	77.30	51.316	77.30	84.304	77.22	20.594	77.28	45.948	77.28
49.033	67.25	52.696	67.25	48.045	67.25	80.805	67.18	17.720	67.22	42.810	67.22
45.425	57.42	49.056	57.42	44.424	57.42	76.949	57.38	14.548	57.41	39.343	57.41
41.284	47.66	44.894	47.65	40.282	47.65	72.515	47.62			35.366	47.68

Ethylbenzene March 9, 1943		o-Xylene March 2, 1943		m-Xylene March 4, 1943		p-Xylene February 3, 1943		n-Propyl- benzene February 24, 1943		Isopropyl- benzene February 25, 1943	
° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg	° C	mm Hg
137.124	779.34	145.367	779.36	140.041	779.36	139.289	779.36	160.202	779.39	153.367	779.39
136.574	767.95	144.809	767.95	139.493	767.95	138.742	768.00	159.625	767.96	152.798	767.96
135.954	755.24	144.176	755.25	138.869	755.25	138.114	755.27	158.972	755.27	152.152	755.27
135.399	744.05	143.614	744.06	138.314	744.06	137.558	744.07	158.389	744.08	151.576	744.08
134.800	732.08	143.007	732.09	137.713	732.09	136.956	732.10	157.760	732.11	150.956	732.11
129.221	627.93	137.346	627.93	132.128	627.93	131.355	627.93	151.903	627.94	145.176	627.94
121.312	500.70	129.318	500.71	124.205	500.70	123.409	500.71	143.598	500.72	136.983	500.72
114.020	402.44	121.909	402.44	116.896	402.44	116.083	402.45	135.942	402.44	129.433	402.44
107.183	324.93	114.965	324.94	110.041	324.94	109.211	324.97	128.764	324.95	122.353	324.95
100.561	261.75	108.227	261.75	103.396	261.75	102.546	261.78	121.807	261.76	115.495	261.76
95.056	217.17	102.632	217.17	97.870	217.17	97.013	217.19	116.032	217.18	109.802	217.18
89.071	175.89	96.541	175.89	91.860	175.89	90.990	175.92	109.744	175.89	103.604	175.89
84.599	149.44	91.987	149.44	87.367	149.44	86.488	149.45	105.046	149.44	98.975	149.44
79.777	124.67	87.081	124.67	82.522	124.67	81.636	124.68	99.986	124.67	93.991	124.67
75.027	103.65	82.242	103.65	77.747	103.65	76.852	103.67	94.993	103.66	89.077	103.66
70.862	87.75	77.993	87.75	73.558	87.74	72.657	87.73	90.622	87.73	84.768	87.73
67.775	77.28	74.857	77.28	70.458	77.28	69.549	77.30	87.383	77.29	81.579	77.29
64.463	67.22	71.481	67.23	67.123	67.23	66.216	67.25	83.909	67.24	78.155	67.24
60.796	57.41	67.746	57.41	63.436	57.41	62.523	57.43	80.064	57.41	74.365	57.41
56.589	47.68	63.460	47.66	59.203	47.67	58.288	47.66	75.646	47.65	70.020	47.65

VI. CORRELATION OF THE DATA WITH THE ANTOINE EQUATION

1. METHOD OF CORRELATION

The simple vapor-pressure equation

$$\log_{10} P = A - (B/T), \quad (1)$$

where T is the absolute temperature in degrees Kelvin, has not proved adequate for the representation of accurate vapor pressure data. A simple modification of eq 1, originally proposed by Antoine [5], is

$$\log_{10} P = A - B/(C + t), \quad (2)$$

where t is the temperature in degrees centigrade. The change is thus equivalent to the substitution of the constant C for the ice point, 273.16°K , in eq 1. The Antoine equation has been discussed in detail in a report by G. W. Thomson [6]. The equation has been used successfully by E. R. Smith to represent precise vapor-pressure data over the range 100 to 1,500 mm [7], and has been used by a number of other workers to represent data of moderate precision at higher pressures [6]. Advantages of the Antoine equation are the small number of constants and the fact that the equation may easily be inverted to yield explicitly the temperature corresponding to a given pressure. In addition, there is reason to believe that extrapolation, especially to higher pressures, by means of the Antoine equation is more reliable than for many other equations commonly used.

All the data obtained in the present investigation have been correlated by means of the Antoine equation, and the results show that the equation is entirely adequate to represent the vapor pressures of a wide variety of hydrocarbon liquids over the range 50 to 800 mm.

The constants of the Antoine equation were adjusted by the method of least squares to fit the experimental data on each compound. Certain advantageous simplifications in the calculations were obtained by rewriting the Antoine equation, eq 2, in a different form. Although this modification simplifies the final calculations, the derivation of the necessary equations is complicated, and will therefore be given in some detail.

Equation 2 may be written in the form

$$(A - \log P)(C + t) - B = 0, \quad (3)$$

or, on multiplying out the left side, and making a transformation to new constants,

$$\begin{array}{ll} a = A & A = a \\ b = (AC - B) & \text{or} \quad B = -(ac + b) \\ c = -C & C = -c \end{array} \quad (4)$$

eq 3 becomes

$$F(P, t; a, b, c) = (at + b + c \log P - t \log P) = 0. \quad (5)$$

Equation 5 is another form of the Antoine equation. It will be observed that eq 5 is linear in the constants a , b , and c , whereas neither eq 2 or eq 3 is linear in A , B , and C . Equation 5 may consequently be fitted to the data by least squares without the necessity of making initial estimates of the constants, as would be necessary for eq 2 or eq 3. However, it is convenient, in using eq 5, to make initial estimates of a , b , and c , in order to reduce the number of significant figures necessary in the subsequent least-squares calculation. The initial approximations, say a_0 , b_0 , and c_0 , may be calculated from three selected experimental points, at a low, an intermediate, and a high pressure. Three simultaneous linear equations of the form of eq 5 are obtained, the solution of which yields a_0 , b_0 , and c_0 . For eq 2 or eq 3, three simultaneous nonlinear equations are obtained, and the solution for A , B , and C is more difficult.

Substitution of a_0 , b_0 , and c_0 in eq 5 yields the function

$$F_0(P, t; a_0, b_0, c_0) = (a_0 t + b_0 + c_0 \log P - t \log P). \quad (6)$$

By adding and subtracting F_0 to eq 5 there is obtained

$$f(P, t; F_0; \alpha, \beta, \gamma) = (\alpha t + \beta + \gamma \log P + F_0) = 0, \quad (7)$$

where

$$\begin{aligned} \alpha &= (a - a_0) \\ \beta &= (b - b_0) \\ \gamma &= (c - c_0) \end{aligned} \quad (8)$$

are the corrections to be added to the initial approximations, a_0 , b_0 , and c_0 , to obtain the final adjusted values a , b , and c .

Equation 7 is the form of the Antoine equation used in setting up the normal equations of the method of least squares. The small quantities α , β , and γ are to be adjusted to minimize the weighted sum of the squares of the residuals,

$$S = \sum w^i (f^i)^2, \quad (9)$$

where f^i is the value of f when P and t are replaced by the experimental values P^i and t^i , and the sum is over all the experimental points. The weight of the i th point, w^i , is defined below. The normal equations, which are three simultaneous linear equations to be solved for α , β , and γ , are [18]

$$\begin{aligned} (\sum_i w^i f_\alpha^i f_\alpha^i) \alpha + (\sum_i w^i f_\alpha^i f_\beta^i) \beta + (\sum_i w^i f_\alpha^i f_\gamma^i) \gamma &= \sum_i w^i f_\alpha^i f_0^i \\ (\sum_i w^i f_\beta^i f_\alpha^i) \alpha + (\sum_i w^i f_\beta^i f_\beta^i) \beta + (\sum_i w^i f_\beta^i f_\gamma^i) \gamma &= \sum_i w^i f_\beta^i f_0^i \\ (\sum_i w^i f_\gamma^i f_\alpha^i) \alpha + (\sum_i w^i f_\gamma^i f_\beta^i) \beta + (\sum_i w^i f_\gamma^i f_\gamma^i) \gamma &= \sum_i w^i f_\gamma^i f_0^i \end{aligned} \quad (10)$$

where

$$\begin{aligned} f_\alpha^i &= (\partial f / \partial \alpha)^i = t^i \\ f_\beta^i &= (\partial f / \partial \beta)^i = 1 \\ f_\gamma^i &= (\partial f / \partial \gamma)^i = \log P^i \end{aligned} \quad (11)$$

and

$$\begin{aligned} f_0^i &= f(P^i, t^i; F_0^i; 0, 0, 0) = F_0^i \\ &= (a_0 t^i + b_0 + c_0 \log P^i - t^i \log P^i). \end{aligned} \quad (12)$$

These quantities are to be evaluated for each experimental point (P^i, t^i) , and the sums in eq 10 are over all the points.

It will be observed that the coefficients (sums) on the left side of the normal equations have a simple form, and do not contain the initial estimates of the constants, as would be the case if the normal equations were set up for eq 2 or eq 3. This is a consequence of the linearity of eq 7 with respect to α , β , and γ , and is the principal advantage of the use of this equation.

It can be seen from eq 5 and eq 12 that the quantities f_0^i which are computed in setting up the normal equations will be small and will

clearly reflect any irregularities in the data. It is therefore possible, by inspection of the quantities f_0^t , to make a preliminary evaluation of the precision of the data before the least squares calculation is carried out.

The weights w (the indices i will be omitted for simplicity) are given by the relation

$$w = (1/\sigma_f^2), \quad (13)$$

where σ_f is the expected standard deviation of the function f , of eq 7, from the value zero. σ_f is calculated from the relation

$$\sigma_f^2 = f_t^2 \sigma_t^2 + f_{\log P}^2 \sigma_{\log P}^2, \quad (14)$$

where σ_t and $\sigma_{\log P}$ are the expected standard deviations (of a single value) of t and $\log P$, and

$$\begin{aligned} f_t &= (\partial f / \partial t) = \alpha + (\partial F_0 / \partial t) = (\alpha + a_0 - \log P) \\ &= (a - \log P) = (A - \log P) \end{aligned} \quad (15)$$

$$\begin{aligned} f_{\log P} &= (\partial f / \partial \log P) = \gamma + (\partial F_0 / \partial \log P) = (\gamma + C_0 - t) \\ &= (c - t) = -(C + t). \end{aligned}$$

As the data approximately satisfy eq 3,

$$f_{\log P} \cong -B/(A - \log P). \quad (16)$$

The weight w can be evaluated only approximately because of the inherent uncertainty in σ_t and $\sigma_{\log P}$. It is therefore permissible to use approximate values of A and B in calculating f_t and $f_{\log P}$. The average value of 6.8 for A and 1,250. for B were used in all the calculations of this report.

$\sigma_{\log P}$ may be replaced by (σ_P/P) , where σ_P is the standard deviation of the pressure. In view of the experimental method, σ_P should be representable by an expression of the form

$$\sigma_P^2 = \sigma_{P_0}^2 + \left(\frac{dP}{dt} \right)_w^2 \sigma_{t_0}^2, \quad (17)$$

where σ_{P_0} is the standard deviation of the pressure in the vapor pressure measurements, σ_{t_0} is the standard deviation of the temperature in the calibration measurements with water, and $(dP/dt)_w$ is the temperature coefficient of the vapor pressure of water at the given pressure. The measure of σ_P adopted was the root-mean-square value of the difference in the observed pressure for successive calibrations at a given contact. It was found that these values of σ_P were satisfactorily represented by eq 17 with $\sigma_{P_0} = \pm 0.06$ mm Hg and $\sigma_{t_0} = \pm 0.003$ degree centigrade. The corresponding values of σ_P vary from ± 0.06 mm Hg at the lowest pressure to ± 0.11 mm Hg at the highest pressure. σ_t in eq 12, the standard deviation of the temperature in the vapor pressure measurements, was also taken as ± 0.003 degree centigrade. Finally, the weights, one weight for each contact (or

pressure), were calculated from eq 13 to 17. The use of this single set of weights for all the calculations reduced considerably the labor of the calculations.

The evaluation of α , β , and γ by the solution of eq 19 completes the least squares calculation. The adjusted values of the constants A , B , and C , to be used in the original form of the Antoine equation, eq 2, are then calculated from eq 4 and eq 8.

It is not difficult to show that the adjusted values of A , B , and C should satisfy the relations

$$\begin{aligned}\sum_i w^i [(A - \log P^i)(C + t^i) - B] t^i &= 0 \\ \sum_i w^i [(A - \log P^i)(C + t^i) - B] &= 0 \\ \sum_i w^i [(A - \log P^i)(C + t^i) - B] \log P^i &= 0.\end{aligned}\tag{18}$$

In practice, these sums are found to be very nearly but not exactly zero, because of the accumulation of numerical errors in the least squares calculation. A readjustment of A , B , and C by using these three relations would be equivalent to a second least squares calculation and equally laborious. However, it is easy to make a final small adjustment of B by using the second relation of eq 18, which is equivalent to a second least squares calculation (minimization of S) in which, however, A and C are held constant. The small correction to be added to B is

$$\sum_i w^i [(A - \log P^i)(C + t^i) - B] / \sum_i w^i.\tag{19}$$

This correction was applied in the present calculations. The final values of A , B , and C are therefore very nearly those which minimize the quantity S .

A simple measure of the precision with which the Antoine equation fits the data on a given compound may be obtained from the weighted sum of the squares of the residuals, S . The quantity S is obtained in the course of the solution of the normal equations, without the necessity of computing the individual residuals for each point. From eq 9 and eq 13, S is given by

$$S = \sum_i (f^i / \sigma_f^i)^2,\tag{20}$$

where f^i is the actual deviation of the function f of eq 7 from zero for the given point (P^i, t^i) , and σ_f^i is the expected deviation calculated from eq 14, with the previously stated values for σ_t and σ_P . (f^i / σ_f^i) is thus the ratio of the actual to the expected error for the given point. Therefore, if the number of points in the given set of data is designated by n ,

$$\rho = (S/n)^{1/2} = \left[\frac{1}{n} \sum_i (f^i / \sigma_f^i)^2 \right]^{1/2}\tag{21}$$

is the root-mean-square value of the ratios of the actual deviations to the expected deviations. The actual deviations, f^i , from the value zero may be a result of errors in the measurement of the temperature and pressure or caused by the failure of the Antoine equation to represent exactly the true pressure-temperature relation. The ratio ρ is an averaged measure of these errors.

2. RESULTS OF THE CORRELATION

The values of the three constants of the Antoine equation for vapor pressures, obtained from the data in table 2 as described in the preceding section, are given in table 3, together with the ranges of pressure and temperature over which the experimental data were obtained (and over which, therefore, the resulting equation for each compound is applicable without loss of accuracy). The values of the boiling point, and the pressure coefficient of the boiling point, at 760.00 mm Hg, calculated from the Antoine equation are also given.

In those cases in which two series of measurements on a single compound are given in table 2, the constants in table 3 were derived from the series of more recent date. The earlier series agrees satisfactorily with the equation in every case.

The last column of table 3 gives, for each compound, the root-mean-square value, ρ , of the ratios of the deviations of the observed points from the Antoine equation to the expected standard deviations. The expected deviations were calculated on the basis of standard deviations (of a single value) of ± 0.003 degree centigrade in the temperature and ± 0.06 to ± 0.11 mm Hg in the pressure, for the lowest and highest pressures, respectively. The values of ρ for the 52 compounds vary from 0.09 to 0.52, while the over-all value of ρ , computed for the total of 913 points on 52 compounds, is 0.33. It seems reasonable to conclude that the over-all standard deviations in the measurements were about ± 0.001 to ± 0.002 degree centigrade in the temperature, and ± 0.02 to ± 0.04 mm Hg in the pressure, although it is not possible to separate unambiguously the errors in temperature and pressure. The expected deviations were arrived at from a study of the deviations in the calibration curves of figure 7. As the actual deviations are considerably smaller, it may be concluded that a large part of the variation in the calibration curves represented true changes in pressure at the contacts, and that interpolation on the calibration curves yielded the pressures with the smaller deviations observed.

TABLE 3.—Summary of the results of the correlation of the experimental data with the Antoine equation for vapor pressures

Compound	Formula	Constants of the Antoine equation $\log_{10} P = A - B/(C+t)$, or $t = B/(A - \log_{10} P) - C$. (P in mm Hg; t in °C).			Normal boiling point at 760 mm Hg	Pressure coefficient dt/dP , at 760 mm Hg	Range of measurement		Measure of precision ΔP
		A	B	C			Pressure	Temperature	
PARAFFINS									
<i>n</i> -Pentane.....	C ₅ H ₁₂	6.87372	1075.816	233.359	°C	<i>deg C/mm Hg</i>	<i>mm Hg</i>	°C	
2-Methylbutane (Isopentane).....	C ₅ H ₁₂	6.78967	1020.012	233.097		0.03856	325 to 780	13.3 to 36.8	0.23
<i>n</i> -Hexane.....	C ₆ H ₁₄	6.87776	1171.530	224.366		.03815	501 to 780	16.3 to 28.6	.11
2-Methylpentane.....	C ₆ H ₁₄	6.83910	1135.410	226.572		.04191	88 to 780	13.0 to 69.5	.41
3-Methylpentane.....	C ₆ H ₁₄	6.84887	1152.368	227.129		.04182	125 to 780	12.8 to 61.1	.10
2, 2-Dimethylbutane.....	C ₆ H ₁₄	6.75483	1081.176	229.343		.04117	217 to 780	15.3 to 64.1	.09
2, 3-Dimethylbutane.....	C ₆ H ₁₄	6.80983	1127.187	228.900		.04173	149 to 780	15.4 to 50.5	.41
<i>n</i> -Heptane.....	C ₇ H ₁₆	6.90342	1268.636	216.951		.04480	48 to 780	14.3 to 58.8	.12
2, 2-Dimethylpentane.....	C ₇ H ₁₆	6.81509	1190.298	223.343		.04394	67 to 780	25.9 to 99.3	.48
3, 3-Dimethylpentane.....	C ₇ H ₁₆	6.81813	1223.543	224.687		.04510	48 to 780	15.3 to 80.1	.39
<i>n</i> -Octane.....	C ₈ H ₁₈	6.92377	1355.126	209.517		.04738	58 to 780	13.4 to 86.9	.36
2-Methylheptane.....	C ₈ H ₁₈	6.91737	1337.468	213.693		.04691	48 to 780	52.9 to 126.6	.49
3-Methylheptane.....	C ₈ H ₁₈	6.89945	1331.530	212.414		.04712	48 to 780	41.7 to 118.5	.40
4-Methylheptane.....	C ₈ H ₁₈	6.90065	1327.661	212.568		.04695	48 to 780	42.7 to 119.8	.38
3-Ethylhexane.....	C ₈ H ₁₈	6.89099	1327.884	212.595		.04719	48 to 780	41.7 to 118.6	.46
2, 2-Dimethylhexane.....	C ₈ H ₁₈	6.83716	1273.594	215.072		.04650	48 to 780	42.1 to 119.4	.37
3, 3-Dimethylhexane.....	C ₈ H ₁₈	6.87004	1315.503	214.157		.04724	48 to 780	31.8 to 107.7	.35
2, 4-Dimethylhexane.....	C ₈ H ₁₈	6.85306	1287.876	214.790		.04664	48 to 780	39.2 to 116.5	.26
2, 5-Dimethylhexane.....	C ₈ H ₁₈	6.85984	1287.274	214.412		.04646	48 to 780	34.1 to 110.3	.31
3, 3-Dimethylhexane.....	C ₈ H ₁₈	6.85122	1307.882	217.439		.04741	48 to 780	34.0 to 110.0	.45
3, 4-Dimethylhexane.....	C ₈ H ₁₈	6.87986	1330.035	214.863		.04752	48 to 780	35.4 to 112.9	.28
2-Methyl-3-ethylpentane.....	C ₈ H ₁₈	6.86358	1318.120	215.306		.04749	48 to 780	40.8 to 118.6	.32
3-Methyl-3-ethylpentane.....	C ₈ H ₁₈	6.86731	1347.209	219.684		.04844	48 to 780	38.9 to 116.6	.43
2, 2, 3-Trimethylpentane.....	C ₈ H ₁₈	6.82546	1294.875	218.420		.04755	48 to 780	40.0 to 119.2	.26
2, 2, 4-Trimethylpentane.....	C ₈ H ₁₈	6.81189	1257.840	220.735		.04651	48 to 780	33.1 to 110.8	.37
2, 3, 3-Trimethylpentane.....	C ₈ H ₁₈	6.84353	1328.046	220.375		.04833	48 to 780	24.4 to 100.1	.32
2, 3, 4-Trimethylpentane.....	C ₈ H ₁₈	6.85396	1315.084	217.526		.04761	48 to 780	36.8 to 115.7	.35
<i>n</i> -Nonane.....	C ₉ H ₂₀	6.94495	1435.158	202.331		.04965	48 to 780	36.6 to 114.4	.29
<i>n</i> -Decane.....	C ₁₀ H ₂₂	6.95367	1501.268	194.480		.05172	57 to 780	70.1 to 151.8	.37
<i>n</i> -Dodecane.....	C ₁₂ H ₂₆	6.98059	1625.928	180.311		.05528	48 to 780	94.5 to 175.1	.40
								126.4 to 217.3	.25

* See footnote at end of table.

TABLE 3.—Summary of the results of the correlation of the experimental data with the Antoine equation for vapor pressures—Continued

Compound	Formula	Constants of the Antoine equation $\log_{10} P = A - B/(C+t)$, or $t = B/(A - \log_{10} P) - C$. (P in mm Hg; t in °C).			Normal boiling point at 760 mm Hg	Pressure coefficient dt/dP , at 760 mm Hg	Range of measurement		Measure of precision ρ
		A	B	C			Pressure	Temperature	
NAPHTHENES									
Cyclopentane.....	C ₅ H ₁₀	6.87798	1119.208	230.738	°C 49.262	deg C/mm 0.04003	mm Hg 217 to 780	°C 15.7 to 50.0	0.26
Methylcyclopentane.....	C ₆ H ₁₂	6.86283	1186.059	226.042	71.812	.04274	88 to 780	15.0 to 72.6	.27
<i>n</i> -Propylcyclopentane.....	C ₈ H ₁₆	6.89887	1380.391	212.610	130.937	.04886	48 to 780	51.7 to 131.9	.52
Isopropylcyclopentane.....	C ₈ H ₁₆	6.88083	1375.564	217.475	126.415	.04913	48 to 780	46.9 to 127.4	.24
Cyclohexane.....	C ₆ H ₁₂	6.84498	1203.526	222.863	80.738	.04376	77 to 780	19.9 to 81.6	.42
Methylcyclohexane.....	C ₇ H ₁₄	6.82689	1272.864	221.630	100.934	.04671	48 to 780	25.6 to 101.8	.29
Ethylcyclohexane.....	C ₈ H ₁₆	6.87041	1384.036	215.128	131.783	.04969	48 to 780	51.4 to 132.7	.29
<i>cis</i> -1, 2-Dimethylcyclohexane.....	C ₈ H ₁₆	6.84164	1369.525	216.040	129.728	.04988	48 to 780	49.2 to 130.7	.24
<i>trans</i> -1, 2-Dimethylcyclohexane.....	C ₈ H ₁₆	6.83722	1356.100	219.342	123.419	.04951	48 to 780	43.5 to 124.4	.28
<i>cis</i> -1, 3-Dimethylcyclohexane.....	C ₈ H ₁₆	6.83866	1345.859	215.598	124.450	.04910	48 to 780	45.2 to 125.4	.18
<i>trans</i> -1, 3-Dimethylcyclohexane.....	C ₈ H ₁₆	6.84293	1340.658	218.281	120.088	.04880	48 to 780	41.3 to 121.0	.23
<i>cis</i> -1, 4-Dimethylcyclohexane.....	C ₈ H ₁₆	6.83699	1347.794	216.360	124.321	.04921	48 to 780	44.9 to 125.3	.23
<i>trans</i> -1, 4-Dimethylcyclohexane.....	C ₈ H ₁₆	6.82180	1332.613	218.791	119.351	.04903	48 to 780	40.3 to 120.3	.17
<i>n</i> -Propylcyclohexane.....	C ₉ H ₁₈	6.88288	1457.640	207.511	156.711	.05201	48 to 780	72.5 to 157.7	.36
AROMATICS									
Benzene.....	C ₆ H ₆	6.89324	1203.835	219.924	80.103	0.04273	57 to 780	14.5 to 80.9	0.24
Toluene.....	C ₇ H ₈	6.95337	1343.943	219.377	110.623	.04630	48 to 780	35.4 to 111.5	.40
Ethylbenzene.....	C ₈ H ₁₀	6.94998	1419.315	212.611	136.187	.04898	48 to 780	56.6 to 137.1	.29
<i>o</i> -Xylene.....	C ₈ H ₁₀	6.99937	1474.969	213.714	144.414	.04969	48 to 780	63.5 to 145.4	.31
<i>m</i> -Xylene.....	C ₈ H ₁₀	7.00343	1458.214	214.609	139.102	.04903	48 to 780	59.2 to 140.0	.32
<i>p</i> -Xylene.....	C ₈ H ₁₀	6.98648	1450.688	214.990	138.348	.04918	48 to 780	58.3 to 139.3	.24
<i>n</i> -Propylbenzene.....	C ₉ H ₁₂	6.95178	1491.548	207.171	159.216	.05143	48 to 780	75.6 to 160.2	.27
Isopropylbenzene.....	C ₉ H ₁₂	6.92929	1455.811	207.202	152.393	.05076	48 to 780	70.0 to 153.4	.29

* See text, section VI.

VII. DISCUSSION

The data obtained in this investigation show clearly several simple correlations between the values of the "B" and "C" constants of the Antoine equation and molecular structure for the compounds of the several classes.

Figures 8 and 9 give plots of the values of the "B" and "C" constants, respectively, of the Antoine equation as a function of the number of carbon atoms in the molecule for several members of the series of normal paraffins, alkylcyclopentanes, alkylcyclohexanes, and alkylbenzenes. From correlations such as these, values of the "B" and "C" constants may be estimated with reasonable certainty for neighboring higher members of these series. With two constants so determined, the normal boiling point would fix the third constant, A,

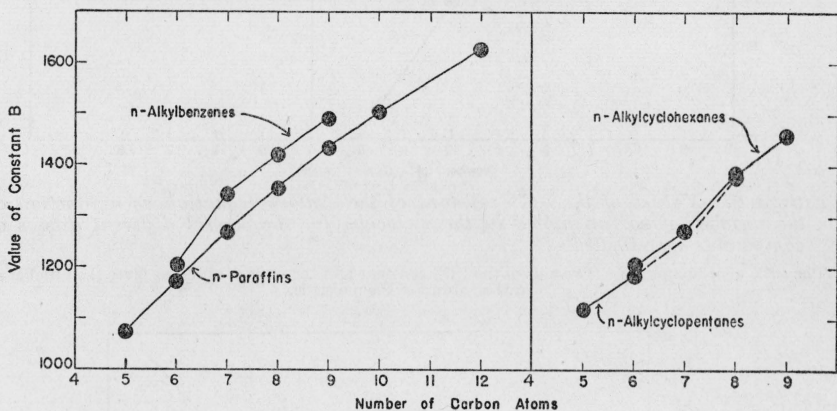


FIGURE 8.—Values of the "B" constant of the Antoine equation as a function of the number of carbon atoms in the molecule, for the several different classes of compounds investigated.

The scale of ordinates gives the value of the "B" constant and the scale of abscissas gives the number of carbon atoms in the molecule.

and thus permit setting up the complete vapor-pressure equation from a knowledge only of the boiling point at one pressure.

Figure 10 gives, from the data on the hexanes, heptanes, and octanes, a plot of the values of the difference, between a normal paraffin and a given isomer, of the "B" constant of the Antoine equation as a function of the difference in the normal boiling point of the two isomers. Figure 11 gives, from the data on the hexanes, heptanes, and octanes, a plot of the values of the difference, between a normal paraffin and a given isomer, of the "C" constant of the Antoine equation as a function of the number of tertiary and quaternary carbon atoms in the molecule. Correlations of this kind make possible the prediction of vapor pressure equations on the basis of one value of the boiling point, which itself may be estimated by a method already described [13].

The usefulness of the data of the present investigation in formulating simple rules in connection with the separation of close-boiling hydrocarbons by distillation at different pressures will be discussed in another report [12].

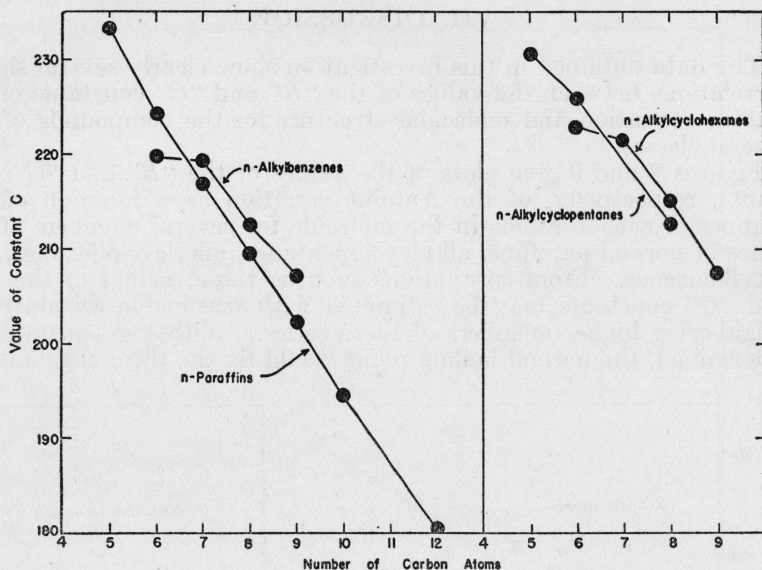


FIGURE 9.—Values of the “C” constant of the Antoine equation as a function of the number of carbon atoms in the molecule, for the several different classes of compounds investigated.

The scale of ordinates gives the value of the “C” constant and the scale of abscissas gives the number of carbon atoms in the molecule.

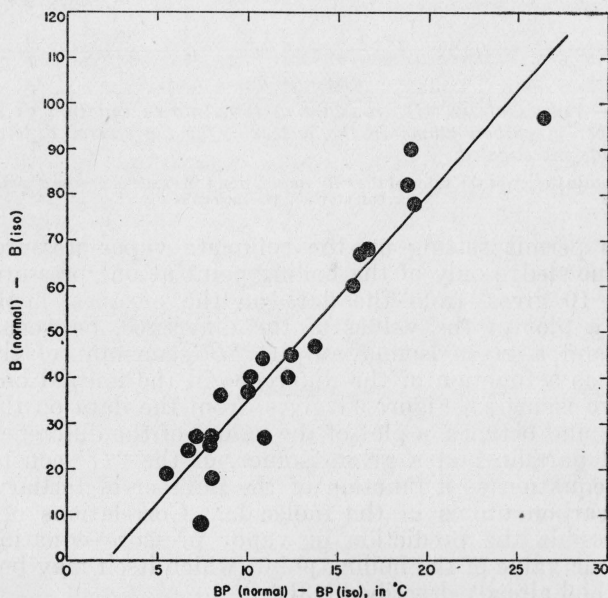


FIGURE 10.—Values of the difference, between a normal paraffin and a given isomer, in the “B” constant of the Antoine equation, as a function of the difference in the normal boiling point of the two isomers.

The scale of ordinates gives the value of the “B” constant for the normal paraffin less that of the isoparaffin. The scale of abscissas gives the value of the normal boiling point of the normal paraffin less that of the isoparaffin. This plot represents the data on the hexanes, heptanes, and octanes.

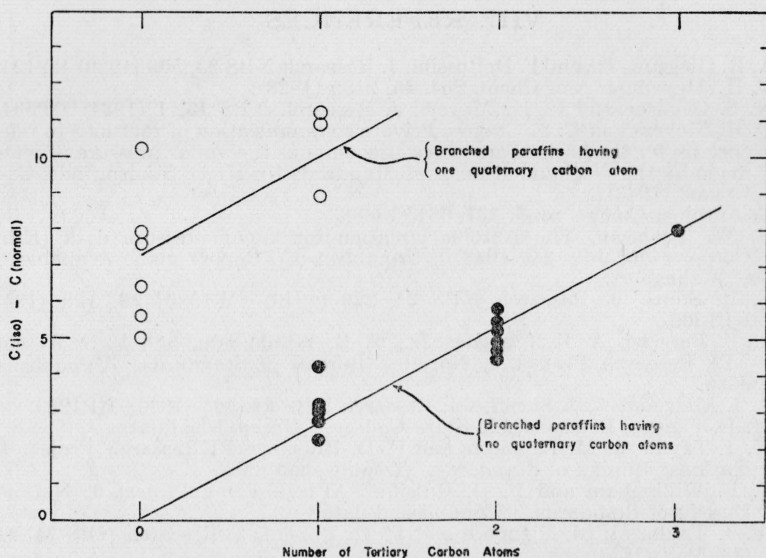


FIGURE 11.—Values of the difference, between a normal paraffin and a given isomer, in the "C" constant of the Antoine equation, as a function of the number of tertiary and quaternary carbon atoms in the molecule.

The scale of ordinates gives the value of the "C" constant for the isoparaffin less that of the normal paraffin. The scale of abscissas gives the number of tertiary carbon atoms in the molecule, with the upper curve applying to those molecules having one quaternary carbon atom and the lower curve to those having no quaternary carbon atoms. This plot represents the data on the hexanes, heptanes, and octanes.

The data of the present investigation are being correlated with existing other vapor pressure data on the same and additional compounds in connection with the work of the American Petroleum Institute Research Project 44 at this Bureau, and a comparison of the present data with data of previous investigations will appear in a report of that work [11]. This latter report will also contain an extension, with detailed discussion, of the various correlations, together with the prediction of vapor-pressure equations for a number of hydrocarbons for which no data are available. The correlations in this latter report are being made according to the method described in another report from this laboratory [13], which involves a consideration of the interaction among various groups in the molecule.

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